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For carbonates of the calcite structure, experimentally measured bulk moduli on NiCO_3 , MgCO_3 , CoCO_3 , FeCO_3 , MnCO_3 , and CaCO_3 have been found to deviate from empirical predictions, in the sense that substitution of alkaline earth elements by the 3d transition metals yields a different bulk modulus-volume relationship (1., 2.). Here we report new compression data on ZnCO_3 and CdCO_3 from in-situ X-ray diffraction, which, in combination with our previous results, completes a systematic study of compressibilities for all calcite-structure carbonates. As known from earlier work, the bulk moduli of the 3d transition metal carbonates show an inverse correlation with room-pressure M-O bond length and volume that is linear. MgCO_3 , however, plots well below the trend, and CaCO_3 slightly below. One particular focus of this work is the contribution of the crystal field to the bulk modulus. No crystal field effect beyond that reflected in the ionic radii is observed among the 3d transition metal carbonates, since ZnCO_3 and MnCO_3 are colinear with NiCO_3 , CoCO_3 and FeCO_3 . Notably, the bulk moduli of ZnCO_3 and CoCO_3 are essentially identical, as are their ambient M-O bond lengths and volumes. The bulk modulus of CdCO_3 , whose ambient M-O bond length and volume are only slightly smaller than those of calcite, is more than 30 GPa greater than that of calcite, and falls about 15 GPa above the trend of the 3d transition metal carbonates. Hence, neither bond-length (or volume) nor crystal-field effect can account for the observed bulk moduli for the complete set of calcite-structure carbonates. Systematic behavior appears to be limited to subsets of carbonates whose metal cations share particular character of their valence electron, e.g., s-type vs. 3d vs. 4d shells.

1. Zhang J and Reeder RJ, Equation of State of Calcite-Structure Carbonates, NSLS Activity Reports, P. B-147, 1996.

2. Zhang J and Reeder RJ, Comparative compressibilities of the calcite-structure carbonates. AGU Spring Meeting, 1997.